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(54) Title: AQUEOUS SUSPENSIONS OF COLLOIDAL PARTICLES, PREPARATION AND USE OF THE SUSPENSIONS (57) Abstract Aqueous suspensions of colloidal particles which particles are both silica based anionic particles and swollen particles of clays of smectite type which are expandable in water and a process for the preparation thereof. The suspensions are useful as flocculating agents and particularly in combination with polymers in the production of paper.		

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Aqueous suspensions of colloidal particles, preparation and use of the suspensions

The present invention relates to aqueous suspensions of colloidal particles which particles are both silica based anionic particles and hydrated particles of clays of smectite type which expand in water. The invention also relates to a process for the production of the suspensions and to the use of these as flocculating agents in combination with amphoteric or cationic polymers, particularly in the production of paper and pulp, but also for water purification.

During recent years systems based on anionic colloidal particles and cationic or amphoteric synthetic or natural polymers have gained an increased use, particularly at the production of paper for increasing retention and dewatering. The anionic colloidal particles have hereby been silica based or have consisted of clay materials such as bentonite. Such systems are for example disclosed in the European patents 41056, 218674 and 0235893. Generally a fairly high amount of bentonite is required while the considerably more expensive silica sols give good results at substantially lower dosages. From the European patent 0310959 it is also known to use both silica sol and bentonite together with cationic starch. The silica sol and the bentonite can hereby be added simultaneously or after each other and it is also indicated that it is possible to mix the bentonite with the silica sol just prior to addition to the stock.

Silica based particles are delivered in the form of aqueous sols of varying dry contents, mainly dependent on the size of the sol particles. Sol particles are essentially spherical. Clay materials, such as for example bentonite, shall be hydrated at use to give the desired effect, and in this form they cannot be supplied as stable aqueous preparations of sufficiently high dry content to be stored and transported. Bentonite is thus handled in powder form and immediately before use the powder is wetted to give the required swelling and high shear forces are necessary to set surfaces free. In contrast to silica particles clay particles have a flake-like structure. Handling of powder materials is not desirable since all handling of powder materials gives

rise to dust problems and dosage problems and since every user needs equipment for wetting.

According to the present invention it has surprisingly been found that it is possible to prepare stable aqueous suspensions which contain both colloidal anionic silica based particles and colloidal hydrated particles of expandable clays of smectite type. The term suspension as such means a system in which small solid particles are essentially uniformly dispersed in a liquid medium. In the present suspensions the different types of colloidal particles, the spherical silica particles and the flake-like clay particles, are thus essentially uniformly dispersed in water. The suspensions according to the invention can have comparatively high dry contents, up to about 40 per cent, and the pre-prepared suspensions can be delivered to the customer who then avoids the above mentioned problems with handling of powder materials. The suspensions have very good effect both in combination with natural and synthetic polymers and are very cost-efficient. Considerably higher effect can be obtained with the suspensions than what could have been expected by the amount of the particles of the respective type in the suspensions. Particularly good effect is obtained when the suspensions are used in combination with synthetic polymers such as cationic polyacrylamide. With suspensions according to the invention silica based particles having a comparatively low specific surface area, ie comparatively high particle size (about 50 to 400 m^2/g , corresponding to about 50 to about 7 nm) can be used with good results. Silica sols with these larger particle sizes have themselves not given sufficiently good results to be commercially used within the field of retention-dewatering.

The present invention thus relates to suspensions as further defined in the claims.

Silica based particles, ie particles based on SiO_2 , which can be used in the present suspensions includes colloidal silica and colloidal aluminium modified silica or aluminium silicate and different types of polysilicic acid. Suitable silica sols are such which are disclosed in the European patent 41056 and the European patent 185068. The colloidal silica in these sols preferably have a specific surface area

of 50-1000 m²/g and more preferably about 100-1000 m²/g. Commercially sols of this type with discrete particles having a specific surface area of about 400-600 m²/g are usually used and the average particle size is usually below 20 nm and most often from about 10 down to about 1 nm. As stated above, the greater particles of this type can also advantageously be used, ie such having a specific surface area of from about 50 to about 400 m²/g. Particularly suitable silica sols are such which have an S-value within the range of from 8 to 45 per cent and which contain silica particles having a specific surface area within the range of from 750 to 1000 m²/g which are surface modified with aluminium to a degree of from 2 to 25 per cent. This type of silica sol is described in the PCT application WO 91/07350. The silica based particles can also originate from sols based on polysilicic acid and hereby it is meant that the silicic acid material is present in the form of very small particles, of the order 1 nm, with a very high specific surface area, above 1000 m²/g and up to about 1700 m²/g, and with a certain degree of aggregate or microgel formation, as disclosed in the European patent application 348366, the European patent application 359552 and the PCT application WO 89/06637. Further, the silica based particles can originate from silica sols having a certain degree of aggregate or microgel formation, corresponding to an S-value from 15 to 40 per cent, containing silica particles, which may be aluminium modified or not aluminium modified, and having a specific surface area within the range from 300 to 700 m²/g, preferably from 400 to 650 m²/g.

The other type of particles which is present in the suspensions of the invention are hydrated particles of clays which are expandable in water and which are of the smectite type. Clays of smectite type are layered silicate minerals and comprise both naturally occurring materials and synthetic materials. The materials can be chemically treated, eg alkali treated. The clays should be dispersible in water and thereby expand so that particles having a large surface area are obtained. Examples of clays of smectite type which are expandable in water and which can be used in the present suspensions are montmorillonite/bentonite, hectorite, beideli-

te, nontronite and saponite. Bentonite is preferred and especially such which is disclosed in the European patent 0235893 which after swelling preferably has a surface area of 400 to 800 m²/g.

5 In the present suspensions the weight ratio of sol particles to clay particles is within the range 20:1 to 1:10, calculated on dry material. The weight ratio is suitably within the range 10:1 to 1:5 and preferably within the range 6:1 to 1:3. The dry content of the suspensions exceeds 5% by
10 weight and can reach 40% by weight. The dry content suitably exceeds 8% by weight. The upper limit is suitably 30% by weight and preferably 25% by weight. The suspensions according to the invention are stable which means that they can be prepared with high dry contents and satisfactory viscosity
15 which means that they can be prepared, stored and transported for later use within time periods which are commercially acceptable. As a measure of the stability it can be mentioned that the viscosity of the suspensions three weeks after their preparation should suitably not exceed 1000 cp, measured with
20 Brookfield viscosimeter DV III, spindle 18, at 30 rpm and at 20°C. It is surprising that stable suspensions according to the invention can be prepared with high contents of hydrated clay material of smectite type. Stable suspensions according to the invention can be prepared without use of protective
25 colloids or dispersing agents and it is assumed that the spherical silica particles to a certain extent will function as dispersing agent for the clay material and prevent the thin, flake-like clay particles from agglomerating. The suspensions contain both silica material and clay material and
30 this means that they have a viscosity considerably below the viscosity for a suspension containing only corresponding amount of clay material. The silica material in the present suspensions thus has a double effect, as dispersing agent and as active substance for the flocculation effect at use. It is
35 an advantage that the present suspensions can be prepared without use of additional chemicals for dispersing since such chemicals may have a negative influence on the flocculation effect at the use of the suspensions. Protective colloids and/or dispersing agents can, however, be used if desired,

particularly for suspensions of higher dry contents. Such agents can for example be of anionic or nonionic character. As examples of suitable protective colloids can be mentioned water soluble cellulose derivatives such as hydroxyethyl- and
5 hydroxypropyl-, methylhydroxypropyl- and ethylhydroxyethyl-cellulose, methyl- and carboxymethylcellulose, gelatin, starch, guar gum, xanthan gum, polyvinyl alcohol etc.. Optional dispersing agents shall be of anionic and/or nonionic character. Anionic dispersing agents can for example be alkyl-
10 or alkylaryl- sulphates, -sulphonates, -ethersulphates, -phosphates or -etherphosphates, polyacrylic acid and salts of polyacrylic acid etc.. Nonionic dispersing agents can for example be ethoxylated fatty alcohols, fatty acids, alkyl phenols or fatty acid amides, ethoxylated or non-ethoxylated
15 glycerol esters, sorbitan esters of fatty acids etc.. The suspension may also contain other additives such as preservative agents.

The suspensions according to the invention can for example be prepared by first mixing the clay with water and
20 then adding the silica based sol before the clay has had time to expand in the water followed by careful dispersing. However, it is preferred that the suspensions are prepared by mixing the clay into a sol of silica based particles followed by careful dispersing in this using high shear forces. The
25 dispersing process can for example be carried out using an Ultra-Turrax or other intensive mixer. For the actual dispersing process times are adjusted with regard to the shear forces which are used. The dispersing can be finished in 10 to 15 minutes but using normal equipment an hour or a couple of
30 hours are as a rule required for the dispersing. At the dispersing the clay particles swell. The pH of the suspensions should suitably not be below 2 and not above 11.

The present suspensions are suitable for use as flocculating agents, for example in the production of pulp and
35 paper and within the field of water purification, both for purification of different kinds of waste water and for purification specifically of white water from pulp and paper industry. The suspensions can be used as flocculating agents in combination with cationic or amphoteric polymers which can

be natural polymers, ie based on carbohydrates, or be synthetic. As examples of suitable polymers can be mentioned cationic and amphoteric starch, cationic and amphoteric guar gum, cationic and amphoteric acrylamide based polymers, 5 cationic polyethyleneimines, polyamidoamines and poly(diallyl-dimethylammonium chloride). Particularly good results have been obtained when the suspensions have been used in combination with cationic polyacrylamide. Even if arbitrary addition order can be used it is preferred that the polymer is 10 added to pulp, stock or water before the suspension.

The preferred field of use for the suspensions, in combination with polymer, is for improvement of retention and dewatering in the production of paper. The suspensions are hereby suitably added in an amount of from 0.05 to 5 kg per 15 ton, calculated as dry on dry stock system, ie fibres and optional fillers, and preferably in an amount of from 0.1 to 3 kg per ton. The dry content of the suspensions at addition to the stock is suitably adjusted to 0.1 to 10 per cent by weight. For synthetic cationic or amphoteric polymers at least 20 0.01 kg of polymer, calculated as dry, per ton of dry stock system is usually used and suitably amounts of from 0.01 to 3 and preferably from 0.03 to 2 kg per ton are used. For carbohydrate based cationic or amphoteric polymers such as starch and guar gum amounts of at least 0.1 kg/ton, calculated 25 as dry on dry stock system, are usually used. For these polymers amounts of from 0.5 to 30 kg/ton are suitably used and preferably from 1 to 15 kg/ton.

The suspensions, in combination with the polymers, can be used in the production of paper from different kinds of 30 stocks of cellulose containing fibres for example stocks from chemical pulp, such as sulphate- and sulphite pulp, chemothermomechanical pulp (CTMP), thermomechanical pulp, refiner pulp or groundwood pulp from both hardwood and softwood and can also be used for stocks based on recycled fibres. The 35 stocks can of course contain mineral fillers of conventional types such as for example kaolin, titanium dioxide, chalk, talc and both natural and synthetic calcium carbonates. Good results have also been obtained with stocks which are usually considered as difficult. Examples of such stocks are those

containing mechanical pulp such as groundwood pulp, stocks based on recycled fibres and stocks which due to the white water system contain high amounts of anionic impurities such as lignin or dissolved organic compounds and/or high contents of electrolytes. Very good results have also been obtained for news furnishes containing recycled fibres and for hydrogen peroxide bleached magazine furnishes. As well known for silica based sols as such an improvement of the retention and dewatering effect can also be obtained for the present suspensions by addition of an aluminium compound to the stock. Any in paper production per se known aluminium compound can be used, for example alum, aluminates, aluminium chloride, aluminium nitrate and polyaluminium compounds, such as polyaluminium chlorides, polyaluminium sulphates and polyaluminium compounds containing both chloride and sulphate ions.

The invention is further illustrated in the following examples which, however, are not intended to limit the same. Parts and per cent relate to parts by weight and per cent by weight respectively, unless otherwise stated.

20 Example 1

Two suspensions, Suspension 1a) and 1b), having dry contents of about 8.7% were prepared from a silica sol and Na-bentonite. The silica sol (Sol 1) was a 8.5% sol with particles having a specific surface area of about 890 m²/g and the particles were aluminium modified to a degree of 7%. The S-value of the sol was 30% and the pH value about 9.2.

Suspension 1a) was prepared from 100 g silica sol, 8.93 g of bentonite and 91.07 g of water. The ratio of aluminium modified silica to bentonite in this suspension was thus about 1:1. The suspension 1b) was prepared starting from 133.3 g of silica sol, 5.95 g of bentonite and 60.72 g of water. The ratio silica to bentonite in this suspension was thus about 2:1. The bentonite was added to the silica sol and dispersion was carried out by means of an Ultraturrax at 10000 rpm during 10 minutes. The viscosity of the suspensions was measured with a Brookfield viscosimeter DV-III (spindle no. 18, 30 rpm). The suspensions were then stored at 55°C for 40 days, which corresponds to storage at room temperature for 400 days. The viscosity was measured after 20 days and 40 days storage.

	Viscosity cp		
	Freshly prepared	20 days	40 days
Suspension 1a	12.2	17.9	25.8
Suspension 1b	8.6	12.0	14.6

5 As evident the suspensions showed only a very slight viscosity change which indicates a very good stability.

Example 2

10 In the same manner as in Example 1 a suspension according to the invention was prepared from 125 g of the same silica sol as in Example 1 and 5 g of Na-bentonite. After about 6 hours the bentonite was entirely dispersed in the sol. This suspension (Suspension 2) thus had a ratio aluminium modified silica to bentonite of 2:1 and a dry content of about 12% by weight. The viscosity, measured as in Example 1, was
15 11.3 cp.

Example 3

20 In corresponding manner as in Example 1 a suspension was prepared from 7 g of Na-bentonite and 93 g of a 15% silica sol (Sol 2) with particles having a specific surface area of about 500 m²/g and in which 9% of the silicon atoms in the surface groups had been replaced by aluminium atoms. After about 10 hours the bentonite was entirely dispersed in the silica sol. The viscosity for this suspension, measured as above, was 33 cp. As a comparison it can be mentioned that a 6% suspension
25 of only bentonite had a viscosity of about 2900 cp and was thus very difficult to handle. The suspension of this example will in the following be referred to as Suspension 3.

Example 4

30 A suspension was prepared by mixing a sol having particles with a surface area of 230 m²/g and containing 29% SiO₂ and 0.3% Al₂O₃ with 11.2 g of bentonite which had been mixed with and hydrated in water. The prepared suspension had a dry content of 10% by weight and a ratio of silica to bentonite of 1:2.

35 Example 5

 In this test the retention effect, retention of fibres and fillers in paper production, of the suspensions 1a) and 1b) after 20 days of storage was investigated and a comparison was made with solely silica sol. A standard stock, based on

pulp with the composition 60% bleached birch sulphate + 40% bleached pine sulphate to which 30% of chalk as a filler and 0.3 g/l of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ had been added, was used. The stock had a concentration of 4.9 g/l and a fine fraction content of 0.376 g/l.

The retention properties, in this and following examples, were evaluated by means of a Britt Dynamic Drainage Jar at 800 rpm. This is the conventional test method for retention in the paper industry. The suspensions were used in amounts of 0.8 kg/t in combination with 4 kg/t of a high cationized starch, containing 0.8% nitrogen. The cationic starch was added before the suspension or the silica sol. The amounts that are given in this and following examples are calculated as dry on dry stock system, ie fibres and fillers.

The suspension 1a) gave a retention of 60.8% and the suspension 1b) gave a retention of 58.8%. Sol 1 gave a retention of 51.8% when added in an amount of 0.5 kg/t and of 55.6% when added in an amount of 0.6 kg/t.

Example 6

In this example the retention effect of the suspension according to Example 2 was investigated. Comparisons were made with a silica sol of the same kind as present in the suspension (sol 1) and with bentonite. The stock was a standard stock with the composition 60% bleached birch sulphate + 40% bleached pine sulphate. 30% of chalk had been added to the pulp as filler and the pulp was then diluted to a concentration of about 5 g/l. 0.3 g/l of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ were then added. The stock had a fines fraction content of 36.6% and a pH of 8.1. The effect of the suspension, the silica sol and the bentonite was investigated in combination with a conventional low cationized starch having a degree of substitution of 0.042 (sold under the name Raisamyl 142) which in all tests was added in an amount of 8.0 kg/ton of dry stock system (fibres + filler).

The tests gave the following retention results:

Suspension 1a in an amount of 1 kg/t: 62.4%.

Sol 1 in an amount of 0.5 kg/t: 47.0%.

The tests with bentonite were made in amounts of 2, 4 and 6 kg/ton respectively and gave the retention results: 34.3%,

42.0% and 48.1% respectively.

Considerably improved results were thus obtained when the suspension according to the invention were added in an amount corresponding to the sol amount when this was added on its own and this when the amount of bentonite mixed into the suspension could not be expected to give any contribution to improvement of the retention.

Example 7

Using exactly the same stock as in Example 5 an investigation of retention was made also with the suspension according to Example 3 and a comparison was made with solely the sol used in this suspension. The same starch as in Example 6 was used and also here in an amount of 8.0 kg/t.

The tests gave the following retention results:

- Suspension 3 in an amount of 2 kg/t: 62.4%.
- Suspension 3 in an amount of 3 kg/t: 73.5%.
- Sol 2 in an amount of 1 kg/t; 48.7%.
- Sol 2 in an amount of 2 kg/t: 69.1%.

Also for this suspension considerably improved results were thus obtained when this was added to give the same sol amount as when the sol was used by itself and this when the amount of bentonite mixed into the suspension could not be expected to give any contribution to improvement of the retention.

Example 8

Retention tests were made with a standard stock (based on pulp of 60% bleached birch sulphate + 40% bleached pine sulphate with addition of 30% of chalk and 0.3 g/l of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$). The stock concentration was about 5 g/l, the fine fraction content was 37.4% and the pH 8.1. In these tests the suspension 2, sol 1 and bentonite were used in combination with a cationic polyacrylamide, Floerger Fo 4190 PG, with 10 mole per cent of cationic charges and a molecular weight of about 10 millions. The cationic polyacrylamide was used in an amount of 1.0 kg/t.

The obtained retention results were as follows:

	Susp. 2 kg/t	Sol 1 kg/t	Retention %
	0.1		48.9
	0.2		58.6
5	0.3		74.2
	0.4		80.0
	0.5		85.0
		0.1	44.6
		0.2	53.7
10		0.3	68.8
		0.4	72.6
		0.5	76.9

Solely bentonite added in an amount of 0.5 kg/t gave a retention of 72.0%.

Thus considerably improved results were obtained also for combinations with cationic polyacrylamide when the suspension was added in an amount corresponding to the same sol amount as when this was used on its own and this when the amount of bentonite mixed into the suspension was such that no contribution to improvement of retention could be expected of this.

Example 9

In this example retention tests were made with the suspension according to Example 4. Comparisons were made with a silica sol of the same kind as in the suspension and with bentonite. In all tests 0.5 kg/t of the same cationic polyacrylamide as utilized earlier was used. The retention tests were made with a standard pulp of the same kind as earlier. The stock had a concentration of about 5 g/l and a fine fraction content of 38.3%.

The retention results were as follows:

Suspension 4 added in an amount of 1.5 kg/t: 69.0%.

Sol 4 added in an amount of 1.0 kg/t: 32.8%.

Bentonite added in amounts of 2, 4 and 6 kg/t respectively: 51.4%, 53.5% and 54.0% respectively.

The sol used in this example had an extremely low surface area and has in itself no positive effect on retention. However, with suspensions containing this sol and bentonite a marked improvement of retention was obtained and

this could not have been expected with regard to the amount of bentonite.

Example 10

In this example a series of suspensions were prepared with varying contents of silica particles and Na-bentonite (White bentonite). The suspensions were prepared by dispersing in a Waring-mixer using maximum rpm during 15 minutes. The silica sols that were used were: sol A = sol with particles having a specific surface area of about 890 m²/g, aluminium modified to a degree of 5%, the S-value for sol A was 30% and the pH was about 8.8; sol B = sol with particles having a specific surface area of 500 m²/g and the particles were aluminium modified to a degree of 9% and the sol was alkali stabilized to a molar ratio SiO₂:Na₂O of about 40:1; sol C = sol corresponding to sol B with the exception that the particles were not aluminium modified; sol D = sol with particles having a specific surface area of 220 m²/g and an aluminium modification of 5% and the sol was alkali stabilized to a molar ratio SiO₂:Na₂O of about 90:1; sol E = sol corresponding to sol D with the exception that the particles were not aluminium modified and that the molar ratio SiO₂:Na₂O was about 100:1.

For the prepared suspensions the viscosity was measured with a Brookfield viscosimeter RVT, spindle 4, 50 rpm at 20°C, 10 days after their preparation. The samples were shaken slightly before measuring.

In table 1 below the composition of the suspensions and the measured viscosities are shown. The ratio Si:B stands for the ratio silica:bentonite in the suspensions, calculated as dry material.

Table 1

	Sol	Dry content	Ratio Si:B	Visc.	
	type	%		cp	
	Susp. a	A	9.6	10:1	10
35	Susp. b	A	10.4	5:1	16
	Susp. c	A	12.7	2:1	60
	Susp. d	A	12.7	1:1	200
	Susp. e	A	12.7	1:2	750
	Susp. f	A	10.0	1:5	600

	Sol	Dry content	Ratio Si:B	Visc.	
	<u>type</u>	<u>%</u>		<u>cp</u>	
	Susp. g	B	21.0	2:1	360
	Susp. h	C	21.0	2:1	130
5	Susp. i	D	25.0	2:1	630
	Susp. j	E	25.0	2:1	620
	Susp. k	E	34.8	5:1	240

As a comparison can be mentioned that while the viscosity of suspension d, which contained 6.3% of bentonite was 200
 10 cp a suspension of solely bentonite with a concentration of 6.3% had a viscosity of about 3000 already 30 minutes after its preparation and was thus classified as a gel.

For certain suspensions the dewatering effect was also investigated by means of a "Canadian Standard Freeness Tester"
 15 which is the conventional method for characterization of dewatering or drainage capability according to SCAN-C 21:65. All additions of chemicals were made at a mixing speed of 1000 rpm. The stock was a standard stock from 60/40 bleached hardwood sulphate pulp and bleached pinewood sulphate pulp
 20 respectively with addition of 30% precipitated calcium carbonate and a concentration of 3 g/l. The dewatering effect for the suspensions was investigated in combination with addition of both cationic starch and cationic polyacrylamide which were added to the stock before the suspensions. The
 25 starch, of the same type as in Example 6, was added in an amount of 10 kg/t and the cationic polyacrylamide, of the same type as in Example 8, in an amount of 0.5kg/t. Additionally 0.5 kg/t of alum were added to the stock first of all. The suspensions were in all cases added in amounts corresponding
 30 to an amount of 0.5 kg/t of silica particles.

Table 2

Suspension	Bentonite amount kg/t	CSF	
	<u>added through the susp.</u>	<u>ml</u>	
35	a	0.05	520
	b	0.1	525
	c	0.25	540
	d	0.5	560
	e	1.0	575
	f	2.5	580

As a comparison can be mentioned that solely sol added in an amount of 0.5 kg silica particles per ton gave a CSF value of 500 and solely bentonite added in an amount of 1 kg/t gave a CSF value of 380. The CSF value of the stock with 5 addition of solely the polymers and alum was 355.

Claims

1. Aqueous stable suspension of colloidal particles, characterized in that the particles are both silica based anionic particles and hydrated particles of clays of smectite
5 type which are expandable in water whereby the weight ratio of silica based particles to clay particles is within the range of from 20:1 to 1:10 and the dry content of the suspension is within the range of from 5 to 40 per cent by weight.

2. Suspension according to claim 1, characterized in
10 that the weight ratio silica based particles to clay particles is within the range of from 6:1 to 1:3.

3. Suspension according to claim 1 or 2, characterized in that the dry content of the suspension is within the range of from 8 to 30 per cent by weight.

15 4. Suspension according to any of the preceding claims, characterized in that the silica based particles originate from a silica based sol having an S-value within the range of from 8 to 45% and having silica particles with a specific surface area within the range from 750 to 1000 m²/g, the
20 particles being aluminium modified to a degree of from 2 to 25%.

5. Suspension according to any of the preceding claims, characterized in that the clay particles are bentonite particles.

25 6. A process for the preparation of an aqueous suspension of colloidal particles, characterized in that a clay of smectite type which is expandable in water is mixed into a sol of silica based particles and dispersed in this for formation of a suspension wherein the weight ratio of silica based
30 particles to clay particles is within the range of from 20:1 to 1:10 and wherein the dry content of the suspension is within the range of from 5 to 40 per cent by weight.

7. Use of an aqueous suspension of colloidal particles which particles are both silica based particles and particles
35 of clay of smectite type which are expandable in water whereby the weight ratio of silica based particles to clay particles in the suspension is within the range of from 20:1 to 1:10 and the dry content of the suspension is within the range from 5 to 40 per cent by weight, as flocculating agent in combination

with cationic or amphoteric polymers in the production of pulp and paper and for water purification.

8. Use according to claim 7, whereby the suspensions are used as flocculating agent for improvement of retention and
5 dewatering in paper making.

9. Use according to claim 7 or 8, whereby the suspensions are used in combination with cationic starch and/or cationic acrylamide based polymer.

10. Use according to claim 9, whereby the suspensions are used in combination with cationic acrylamide based polymer.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 93/00664

A. CLASSIFICATION OF SUBJECT MATTER

IPC5: C01B 33/14, C02F 1/52, D21H 17/68, D21H 21/10
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

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IPC5: C01B, C02F, D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP, A1, 0310959 (HOKUETSU PAPER MILLS, LTD), 12 April 1989 (12.04.89), abstract --	1-10
A	WO, A2, 9003330 (PPG INDUSTRIES, INC.), 5 April 1990 (05.04.90), abstract -- -----	1-10

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "B" earlier document but published on or after the international filing date
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- "P" document published prior to the international filing date but later than the priority date claimed

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Date of the actual completion of the international search

26 November 1993

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INTERNATIONAL SEARCH REPORT
Information on patent family members

01/10/93

International application No.

PCT/SE 93/00664

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A1- 0310959	12/04/89	SE-T3- 0310959 CA-A- 1301413 JP-A- 1092498 JP-B- 4024477 US-A- 4902382	26/05/92 11/04/89 27/04/92 20/02/90
WO-A2- 9003330	05/04/90	CN-A- 1050364 EP-A- 0435936 JP-T- 4500500 JP-B- 5007325 US-A- 5030286	03/04/91 10/07/91 30/01/92 28/01/93 09/07/91